

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-140428

(43)Date of publication of application : 08.06.1993

(51)Int.Cl.

C08L 67/02  
C08K 3/00  
//(C08L 67/02  
C08L 25:00 )

(21)Application number : 03-328316

(71)Applicant : TONEN CHEM CORP

(22)Date of filing : 18.11.1991

(72)Inventor : SEZUME TADASHI  
YAGI YUKIHIKO  
EZURE NORIMASA

(54) POLYESTER RESIN COMPOSITION

(57)Abstract:

PURPOSE: To provide the subject compsn. excellent in the balance among stiffness, strengths, heat resistance, and impact resistance.

CONSTITUTION: The objective compsn. comprises 50-95wt.% polyester, 1-40wt.% thermoplastic styrenic elastomer modified with an unsatd. glycidyl compd., and 4-45wt.% inorg. filler.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1] (a) The polyester resin constituent with which polyester, the styrene thermoplastic elastomer which denaturalized with (b) partial saturation glycidyl compound, and (c) inorganic filler are contained, and the rate of said component (a), (b), and (c) is characterized by being (a) 50-95 % of the weight, (b) 1-40 % of the weight, and (c) 4-45 % of the weight, respectively.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a polyester resin constituent. In more detail, it excels in rigidity, reinforcement, thermal resistance, and shock resistance, and is related with a polyester resin constituent suitable as objects for mold goods, such as inner exterior equipment, and an electric equipment article or home electronics of an automobile, etc.

[0002]

[Description of the Prior Art] Polyester is resin excellent in thermal resistance, a mechanical strength, and insulation, and is widely used centering on the electric equipment article taking advantage of the property. However, impact strength of polyester is low, therefore there is a problem in using for the application which also needs shock resistance in addition to the above-mentioned property. Then, although impact strength will increase if thermoplastic elastomer is added in polyester in order to raise the shock resistance of polyester, the rigidity which is the property of polyester, reinforcement, thermal resistance, etc. will fall reversely greatly. Moreover, although rigidity, reinforcement, and thermal resistance will increase if an inorganic filler is added, impact strength will fall greatly. Therefore, the object of this invention is to offer the polyester resin constituent which unites rigidity, reinforcement, thermal resistance, and impact strength with sufficient balance, and has them.

[0003]

[Means for Solving the Problem] this invention persons will reach [ that the polyester resin constituent with which rigidity, reinforcement, thermal resistance, and impact strength have been improved is obtained, and ] a header and this invention, if the styrene thermoplastic elastomer and the inorganic filler which denaturalized with the partial saturation glycidyl compound are blended with polyester at a specific rate as a result of repeating examination wholeheartedly. That is, this invention contains (a) polyester, the styrene thermoplastic elastomer which denaturalized with (b) partial saturation glycidyl compound, and (c) inorganic filler, and it is the polyester resin constituent characterized by the rates of said component (a), (b), and (c) being (a) 50-95 % of the weight, (b) 1-40 % of the weight, and (c) 4-45 % of the weight, respectively.

[0004] Hereafter, the polyester resin constituent of this invention is explained to a detail. (a) polyester of the polyester resin constituent component of this invention is thermoplastics generally obtained by the polycondensation of saturation dicarboxylic acid and saturation dihydric alcohol, for example, polyethylene terephthalate, polypropylene terephthalate, polytetramethylene terephthalate (polybutylene terephthalate), polyhexamethylene terephthalate, polycyclohexane -1, 4-dimethylol terephthalate, poly neopentyl terephthalate, etc. are mentioned. In these, polyethylene terephthalate and polybutylene terephthalate are desirable.

[0005] the intrinsic viscosity  $[\eta]$  (dl/g) which asked for the polyester as the above-mentioned component (a) from the solution viscosity measured at 25 degrees C in the o-chlorophenol solvent -- 0.30-1.8 it is -- the concentration of an end carboxyl group -- 10-200 -- what is m Eq/kg is desirable. the case of polyethylene terephthalate -- intrinsic viscosity  $[\eta]$  -- 0.30-1.2 it is -- end carboxyl group

concentration -- 10-200 -- a m Eq [ /kg ] thing is desirable. In addition, the terephthalic-acid component in polyethylene terephthalate could be permuted by the alkyl group, the halogen radical, etc., and the glycol component may contain other glycols, 1 [ for example, ], 4-butylene glycol, propylene glycol, hexamethylene glycol, etc. to about 50 % of the weight other than ethylene glycol. moreover, the case of polybutylene terephthalate -- intrinsic viscosity [eta] -- 0.30-1.8 it is -- end carboxyl group concentration -- 10-200 -- a m Eq [ /kg ] thing is desirable. Also in this case, the terephthalic-acid component could be permuted by the alkyl group, the halogen radical, etc., and the glycol component may contain other glycols, for example, ethylene glycol, propylene glycol, hexamethylene glycol, etc. to about 50 % of the weight other than 1 and 4-butylene glycol.

[0006] The styrene thermoplastic elastomer which denaturalizes with the partial saturation glycidyl compound in the (b) component of the polyester resin constituent of this invention is the water garnish of copolymers, such as random of a styrene system monomer and other monomers, such as a styrene system monomer, a monoolefin which may be copolymerized, or a diolefin, a block, and a graft, and these copolymers.

[0007] Here, as a styrene system monomer, they are styrene, alpha-chloro styrene, 2, 4-dichloro styrene, p-methoxy styrene, p-methyl styrene, p-phenyl styrene, p-divinylbenzene, and p. -(chloro methoxy)-Styrene, alpha methyl styrene, o-methyl-alpha methyl styrene, m-methyl-alpha methyl styrene, p-methyl-alpha methyl styrene, p-methoxy-alpha methyl styrene, etc. are mentioned. In these, styrene is used preferably.

[0008] As a diolefin which is made to carry out copolymerization to the above-mentioned styrene system monomer, and is made into a styrene thermoplastic elastomer, conjugated dienes, such as nonconjugated diene, such as a dicyclopentadiene, 1, 4-hexadiene, cyclo-octadiene, and methyl norbornene, or a butadiene, and an isoprene, are mentioned, for example. In these, a butadiene and an isoprene are desirable. Moreover, as a monoolefin, a with a carbon numbers [ of a propylene besides ethylene, butene-1, a hexene -1, the 3-methylbutene -1, the 4-methyl-pentene -1, a heptene -1, octene -1, and decene-1 grade ] of three or more alpha olefin is mentioned, and ethylene and a propylene are desirable in these.

[0009] The styrene thermoplastic elastomer used as a raw material elastomer of a denaturation styrene thermoplastic elastomer in the component (b) of this invention can be obtained by copolymerizing by the suitable approach, for example, the anionic polymerization, and radical polymerization of common knowledge of the suitable above-mentioned monomer. As an example of a desirable raw material elastomer The styrene-ethylene-butylene-styrene block copolymer which are a styrene-butadiene-styrene block copolymer (SBS) and its water garnish (SEBS), A styrene-butadiene copolymer (SB) and its water garnish, a styrene-ethylene-butylene block copolymer (SEB), A styrene-isoprene copolymer (SI) and its water garnish, a styrene-ethylene-propylene block copolymer (SEP), The styrene-ethylene-propylene-styrene block copolymer (SEPS) which are a styrene-isoprene-styrene block copolymer (SIS) and its water garnish is mentioned, and SEBS and SEPS are desirable especially in these.

[0010] The above-mentioned raw material elastomer has that good whose content of a styrene system monomer is 5 - 65 % of the weight, and 15 - 50% of the weight of its thing is especially desirable. Such a desirable raw material styrene thermoplastic elastomer can use a commercial thing, choosing it suitably.

[0011] The component (b) of the polyester resin constituent of this invention denaturalizes the various above-mentioned styrene thermoplastic elastomers with a partial saturation glycidyl compound. As a partial saturation glycidyl compound used as a modifier, the glycidyl compound which has an olefin, the partial saturation radical which may be copolymerized, and a glycidyloxy radical mentions into a molecule here, and it is \*\*\*\*. Unsaturated-carboxylic-acid glycidyl ester, partial saturation glycidylethers, etc. are mentioned, and, specifically, unsaturated-carboxylic-acid glycidyl ester is used preferably. As unsaturated-carboxylic-acid glycidyl ester, for example, the glycidyl ester of unsaturated carboxylic acid, such as an acrylic acid, a methacrylic acid, a crotonic acid, isocrotonic acid, tiglic acid, and angelic acid, is mentioned, and glycidyl acrylate (GA) and glycidyl methacrylate (GMA) are desirable especially.

[0012] In this invention, desirable denaturation thermoplastic elastomer is the above-mentioned raw material styrene thermoplastic elastomer and the thing which denaturalized SEBS or SEPS with said glycidyl compound especially. although the content of the partial saturation glycidyl compound as a modifier of the above-mentioned denaturation styrene thermoplastic elastomer changes with classes of raw material styrene thermoplastic elastomer etc. and does not generally have \*\*\*\*\* -- general -- about 0.2 - 5 % of the weight -- desirable -- It is 0.5 - 3 % of the weight.

[0013] Such a denaturation styrene thermoplastic elastomer can be obtained using known degeneration methods, such as a solution method or the melting kneading method. Moreover, the selection activity of the desired thing may be suitably carried out from a commercial thing. As an example of a degeneration method, the example of denaturation of SEBS by GMA (graft polymerization) is shown below. That is, in the melting kneading method, these components are supplied to an extruder, a 2 shaft kneading machine, etc. using a catalyst SEBS, GMA, and if needed, heating and fusing in temperature of about 170-300 degrees C, it kneads about 0.1 to 20 minutes, and Denaturation SEBS is acquired. Moreover, in the case of a solution method, the above-mentioned starting material is dissolved in organic solvents, such as a xylene, and it denaturalizes, agitating at the temperature of about 90-200 degrees C for 0.1 to 100 hours.

[0014] In any case of a degeneration method, the usual catalyst for radical polymerizations is received as a catalyst at the glycidyl compound 100 weight section for denaturation. It can use a 0.1-10 weight section grade. For example, peroxides, such as benzoyl-peroxide, lauroyl peroxide, peroxidation G t-butyl, acetyl-peroxide, perbenzoic-acid t-butyl, peroxidation JIKUMIRU, perbenzoic-acid, peracetic-acid, and fault pivalate t-butyl, 2, 5-dimethyl -2, and 5-G t-butyl par OKISHIHEKISHIN, and diazo compounds, such as azobisisobutyronitril, are used. In addition, it is also possible to add a phenol system and the Lynn system antioxidant to the above-mentioned graft reaction time.

[0015] In this way, the rate of a graft of the denaturation styrene thermoplastic elastomer obtained is about 0.2 - 5 % of the weight, has 0.1-100g / melt flow rate for about 10 minutes (MFR, JISK7210, 2.16kg of loads, 230 degrees C), and is preferably used by this invention.

[0016] Furthermore by this invention, (c) inorganic filler is blended for an improvement of the rigidity of polyester, reinforcement, and thermal resistance. As an inorganic filler, for example Oxides, such as an alumina, a magnesium oxide, and a calcium oxide, An aluminum hydroxide, a magnesium hydroxide, basic magnesium carbonate, Hydration metallic oxides, such as a calcium hydroxide, a tin-oxide hydrate, and a zirconium dioxide hydrate, Silicates, such as carbonates, such as a calcium carbonate and a magnesium carbonate, talc, clay, and a bentonite, Metal powders, such as sulfates, such as phosphate, such as borates, such as boric-acid barium and boric-acid zinc, aluminium phosphate, and sodium tripolyphosphate, barium, and gypsum, a sulfite, copper, iron, and lead, wollastonite, a mica, these two or more sorts of mixture, etc. are mentioned. These inorganic fillers can use the thing of various configurations, such as the shape of powder, a globular shape, and a flake.

[0017] In the above-mentioned inorganic filler, talc, a barium sulfate, a calcium carbonate, wollastonite, and a mica are desirable, and talc, a calcium carbonate, and a mica are desirable especially. Here, talc is the compound salt of a magnesium oxide and a silicic acid, mean particle diameter of a thing is desirable about 0.1-100 micrometers, and mean particle diameter a calcium carbonate What is about 0.1-30 micrometers is desirable. Moreover, a mica is an aluminosilicate containing alkali metal and that [ its ] whose aspect ratio mean particle diameter is ten to about 500 in about 5-500 micrometers is desirable.

[0018] For the blending ratio of coal of the above-mentioned component (a), (b), and (c), a component (a) is [ the component (c) of a component (b) ] 5 - 30 % of the weight four to 45% of the weight three to 20% of the weight one to 40% of the weight 60 to 90% of the weight preferably 50 to 95% of the weight. If polyester has too few components (a) at less than 50 % of the weight and they exceed 95 % of the weight, the improvement effect of the physical properties of the polyester by the component (b) and (c) will not be accepted.

[0019] Other crystalline polyolefines and polyolefine system elastomers (it is 1 - 20 % of the weight to the whole polyester constituent) may be added to extent which does not spoil the property of the polyester resin constituent of this invention. Here, an olefin system elastomer means the copolymer of

two sorts or three sorts or more of copolymer rubber of the alpha olefin of ethylene, a propylene, butene-1, a hexene -1, and 4-methyl-pentene-1 grade or an alpha olefin, and an other type monomer. As an example of two sorts or three sorts or more of copolymer rubber of the above-mentioned alpha olefin, ethylene-propylene rubber (EPR), ethylene-butene rubber (EBR), and ethylene-propylene-diene rubber (EPDM) can be mentioned. In this invention, other fillers usually further used in the field of the resin constituent for the purpose of the refining besides the above-mentioned matter, reinforcement, a thermostabilizer, light stabilizer, a flame retarder, a plasticizer, an antistatic agent, a foaming agent, a nucleating agent, etc. can be blended suitably.

[0020] The polyester resin constituent of this invention can obtain the 230-320 degrees C of each above-mentioned component using kneading machines, such as a 1 shaft extruder, a twin screw extruder, a Banbury mixer, a kneading roll, and Brabender, by carrying out heating melting kneading at 250-280 degrees C preferably. After there being especially no limit in the kneading sequence of each component in this invention, and carrying out package kneading of a component (a), a component (b), and the component (c) and kneading a component (a) and a component (b), a component (c) may be kneaded and other kneading sequence can also be taken.

[0021]

[Example] Hereafter, an example and the example of a comparison explain this invention to a detail further. In addition, in each example and the example of a comparison, the following were used as a raw material and an additive.

Polyester polybutylene terephthalate PBT: [ TRB-J by Teijin, Ltd. and intrinsic viscosity [eta] 0.87 (inside of o-chlorophenol)]

Styrene thermoplastic elastomer SEBS:[-- the Asahi Chemical Co., Ltd. make -- tough -- melt flow rate (MFR, 190-degree-C, 2.16kg load) 5.0 g / [ tech H-1041, 30 % of the weight of styrene contents, and ] 10-minute]

[0022] denaturation -- a styrene thermoplastic elastomer -- denaturation -- SEBS:SEBS -- [-- Asahi Chemical -- incorporated company -- make -- tough -- a tech -- -- H - 1041 -- styrene -- a content -- 30 -- % of the weight -- a melt flow rate (MFR, 190 degrees C, 2.16kg load) -- 5.0 -- g -- /-- ten -- a minute --] -- 100 -- weight -- the section -- GMA -- 1.5 The weight section and catalyst (par hexyne 25B: Nippon Oil & Fats Co., Ltd. make) The 0.03 weight sections After carrying out dryblend, a 1 shaft extruder with a diameter of 65mm is used for this, and they are 200 degrees C and 100rpm. Melting kneading was carried out on conditions and the GMA denaturation SEBS for melt flow rate (MFR, 230-degree-C, 2.16kg load) 5g / 10 minutes was acquired. The rate of a graft of GMA of this denaturation styrene thermoplastic elastomer was 1 % of the weight.

[0023] Inorganic filler \*\* talc : [Fuji talc incorporated company make, LMS 300, and the mean particle diameter of 1.2 micrometers]

\*\* Calcium carbonate : [the Shiroishi Industries make and HOWAITON P-30]

\*\* Mica : [Kuraray Co., Ltd. make, 200HK, and average flake 90micrometer]

[0024] They are 250 degrees C and 200rpm by the twin screw extruder (ratio-of-length-to-diameter=28) with a diameter [ after carrying out dryblend with a Henschel mixer at a rate which shows one to examples 1-4 and example of comparison 3 polyester (PBT), SEBS which is not denaturalized / the GMA denaturation SEBS (denaturation SEBS) or /, and an inorganic filler (\*\*, \*\*, or \*\*) in the 1st table ] of 45mm. It kneaded and the pellet of a resin constituent was obtained. Thus, the obtained polyester resin constituent was injection molded and the bending elastic modulus, the \*\*\*\* yield point reinforcement, the \*\*\*\* fracture point ductility, heat deflection temperature, and Izod impactive strength of mold goods were measured. A result is shown according to the 1st table.

[0025]

[A table 1]

第 1 表

		実 施 例							比 較 例		
		1	2	3	4	5	6		1	2	3
* 組	ポリエステル	75	75	75	60	75	50		90	85	75
	スチレン系熱可塑性	10	10	10	10	5	20		10		
	エラストマー										10
	未変性SEBS										
成	①タルク	15			30	15	30			15	15
	②炭酸カルシウム		15								
	③マイカ			15							
物 性	曲げ弾性率 (kgf/cm <sup>2</sup> )	20000	19000	20000	21000	21000	19000		19500	40000	20000
	引張降伏点強度 (kgf/cm <sup>2</sup> )	480	470	480	485	490	450		480	660	460
	引張破断点伸度 (%)	80	>300	120	50	70	150		>300	5	30
	熱変形温度 (°C, 荷重4.8kg/cm <sup>2</sup> )	158	140	154	160	160	156		137	190	150
	アイゾット衝撃強度 ( kgf・cm/cm )	65	62	60	18	35	42		9	3	10
		12	15	13	7	10	11		6	3	5

注) \* : 重量%

[0026] The measuring method of each physical properties shown in the 1st table of the above is as follows.

(1) Bending elastic modulus (23 degrees C) : measure by ASTM D-790.

(2) \*\*\*\* yield point reinforcement (23 degrees C) : measure by ASTM D-638.



- (3) \*\*\*\* fracture point ductility (23 degrees C) : measure by ASTM D-638.
- (4) Heat deflection temperature (4.6kg/cm2 of loads) : measure by ASTM D-648.
- (5) Izod impactive strength (23 degrees C and -20 degrees C) : measure by ASTM D-256.

[0027] this invention constituent (examples 1-4) which blended polyester, the GMA denaturation SEBS and talc, the calcium carbonate, or the mica so that clearly from the 1st table The constituent which consists of polyester and GMA denaturation SEBS (example 1 of a comparison), It compares with the constituent (example 3 of a comparison) which consists of the constituent (example 2 of a comparison) and polyester which consist of polyester and an inorganic filler (talc), and Native SEBS and an inorganic filler (talc). It excels in the balance of a bending modulus of elasticity, \*\*\*\* yield point reinforcement, \*\*\*\* fracture point ductility, heat deflection temperature, and Izod impactive strength. Especially an improvement of Izod impactive strength is remarkable.

[0028]

[Effect of the Invention] As explained in full detail above, the polyester resin constituent of this invention blends a denaturation styrene thermoplastic elastomer and an inorganic filler with polyester, and becomes it, and they are rigidity, reinforcement, and the resin constituent excellent in heat-resistant and shock-proof balance. Such a polyester resin constituent especially of this invention is suitable as various engineering plastics as resin constituents of business, such as an inner package of an automobile and exterior parts, and household-electric-appliances components.

---

[Translation done.]